

A
Thesis
On

CHARACTERIZATIONS OF BNT CERAMICS SYNTHESIZED BY DIFFERENT TECHNIQUES

By
Tynee Bhowmick

Under the Supervision
Of
Dr. Pawan Kumar

Department of Physics
National Institute of Technology, Rourkela

Thesis submitted
in partial fulfillment for the Degree of
MASTER OF SCIENCE IN PHYSICS



Department of Physics
National Institute of Technology, Rourkela
Orissa-769008
2010

**Department of Physics
National Institute of Technology, Rourkela
Orissa**

Certificate from the Supervisor

This is to certify that the thesis entitled, “*Characterizations of BNT ceramics synthesized by different techniques*” prepared by **Ms. Tynee Bhowmick** , Roll No: 409PH2085 of Department of Physics of **National Institute of Technology, Rourkela**, for the partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN PHYSICS, at NIT, Rourkela**, is absolutely based upon the research work carried out by her under my supervision and guidance.

To the best of my knowledge, these results have not been submitted by her for the award of any other degree or diploma.

Dr. Pawan Kumar
Dept. of Physics
National Institute of Technology
Rourkela, Orissa

ACKNOWLEDGEMENT

My deepest regards to my guide and supervisor, Dr. Pawan Kumar. Without his kind guidance, I would not have completed my annual project successfully. I also wish to thank all the Phd scholars at Electroceramic Laboratory, Dept. of Physics, National Institute of Technology, Rourkela for extending a helping hand and enlightening me with knowledge during the course of my project work. A special mention, however, has to be made of Prakash *bhai* who supervised over our work from the very beginning till the end, and helping with his kind guidance and support whenever we needed his help. Last, but not the least, my sincere thanks goes out to my classmate and close friend, Mallika Bhattacharyya without whom I would not have taken the first step in the completion of this thesis work.

Tynee Bhowmick

Department of Physics

National Institute of Technology, Rourkela

Orissa-769008

ABSTRACT

Bismuth Sodium Titanate ($\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$) was prepared by the conventional solid state route as well as the chemical route. Calcination of the sample prepared through the solid state route was done at 750°C for 8 hours and of the sample prepared through the chemical route at 600°C for 6 hours. XRD of the samples was done in which a single perovskite phase was confirmed. The samples were sintered using the conventional sintering method at 1150°C for two hours and using the microwave sintering method at 1150°C for 30 minutes with a heating rate of $40^\circ/\text{min}$. SEM images of the samples were taken which showed dense microstructure and uniform grain size. Comparative study of dielectric properties of the samples was done. PE loop measurements were done to confirm the ferroelectric nature of the sample.

Contents

1	INTRODUCTION TO DIELECTRICS AND FERROELECTRICS	3
1.1	Dielectrics	3
1.1.1	Polarization	3
1.1.2	Frequency dependence of dielectrics	4
1.1.3	Dielectric relaxation	4
1.2	Ferroelectrics	5
1.2.1	Types of ferroelectrics	5
1.3	Properties of ferroelectrics	6
1.3.1	Crystal symmetry	6
1.3.2	Piezoelectric effect	6
1.3.3	Spontaneous polarization and pyroelectric effect	8
1.3.4	P-E hysteresis loop - an important criterion for ferro- electricity	8
1.3.5	Phase transition in ferroelectrics	9
1.3.6	Structure of ferroelectrics	10
2	MATERIAL SELECTION	13
2.1	Literature review	13
2.2	Reasons for selection of BNT	13
3	OPTIMIZATION OF SYNTHESIS ROUTES AND EXPER- IMENTAL TECHNIQUES	13
3.1	Solid state synthesis	14
3.1.1	Selection of raw materials	14
3.1.2	Stoichiometric weighing	14
3.1.3	Mixing	14
3.1.4	Calcination	14
3.1.5	Grinding	15
3.1.6	Binder addition	15
3.1.7	Shaping	15
3.1.8	Binder burn out	15
3.1.9	Sintering	15
3.1.10	Electroding	16
3.2	Chemical synthesis	17
3.2.1	Selection of raw materials	17
3.2.2	Stoichiometric weighing	17
3.2.3	Dissolution	17
3.2.4	Mixing of constituents and drying	17

3.3	X-ray diffraction	18
3.4	Scanning electron microscopy	18
3.5	Study of dielectric properties	19
3.6	PE loop	20
4	EXPERIMENTAL PROCEDURE	21
5	RESULTS AND DISCUSSIONS	22
5.1	X-ray diffraction studies	22
5.2	Scanning electron microscopy	23
5.3	Dielectric measurements	23
5.4	PE loop measurements	26
6	CONCLUSIONS	26

1 INTRODUCTION TO DIELECTRICS AND FERROELECTRICS

The recent advances in ceramic technology has brought about a revolution in the digital world. Research in the field of dielectrics is leading to newer inventions each day. However, to understand the hidden capacities of a dielectric material, the first thing that comes to one's mind is what a dielectric exactly is. A brief introduction to the theory of ferroelectrics as well as dielectrics is addressed in the sections that follow.

1.1 Dielectrics

Dielectrics are basically insulators that can be polarized by the application of electric field. When a dielectric material is placed in an electric field, electric charges do not flow through it (like in conductors) but shift from their average equilibrium positions causing polarization. The amount of polarization caused is described by a dimensionless quantity called the dielectric constant.

1.1.1 Polarization

On placing in an electric field, the positive and negative charges of a dielectric are displaced from their equilibrium positions by very small distances throughout the volume of the dielectric. This results in the formation of a large number of dipoles each having some dipole moment in the direction of the field. The material is said to be polarized with a polarization \mathbf{P} . The polarization is defined as dipole moment per unit volume.

Types of polarization:

1. **Electronic polarization:** This type of polarization arises due to the displacement of the electron cloud of an atom relative to its nucleus in the presence of an applied electric field. The polarization as well as the dielectric constant of a material at optical frequencies results mainly from electronic polarization.
2. **Ionic polarization:** Ionic polarization arises due to displacement of a charged ion relative to other ions in a solid. The ionic contribution is important at low frequencies.
3. **Dipolar polarization:** The dipolar polarization arises due to polar substances that can orient themselves in the presence of an external

electric field. The thermal agitation of the molecules tends to counteract the ordering effect of the electric field and an equilibrium state is reached wherein the different dipoles make all possible angles varying from zero to π radians with the field direction.

4. **Space charge polarization:** Space charge polarization arises due to the accumulation of charges at the interface or at the grain boundary of a polycrystalline material. The ions diffuse over appreciable distances in response to the applied field giving rise to re-distribution of charges in the dielectric medium.

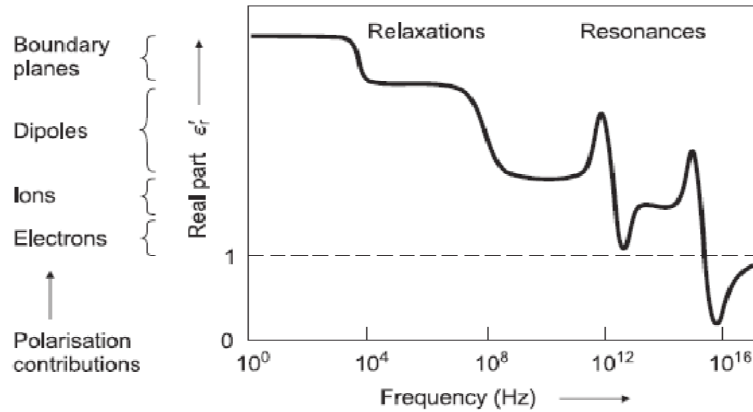


Figure 1: Variation of polarization with frequency

1.1.2 Frequency dependence of dielectrics

Dielectric constant, ϵ_r , of a dielectric material decreases with increase in frequency. The dielectric loss at low frequencies is mainly due to d.c. resistivity. But at high frequencies the dielectric loss is mostly due to dipole rotations or due to ionic transitions from the lower energy states to higher energy states. Because of the upward transition, the energy is absorbed from the applied field. The absorption of energy is possible if orientational polarization or permanent dipole moments are present.

1.1.3 Dielectric relaxation

Dielectrics take a finite time for the polarization to reach its maximum value. This is due to the forces between adjacent molecules which tend to prevent

the alignment along the external field. This phenomenon is called dielectric relaxation. It is an inherent property of relaxor ferroelectrics.

1.2 Ferroelectrics

Ferroelectricity was originally discovered by Valasek in Rochelle salt. Ferroelectrics are dielectric materials that show spontaneous polarization, i.e., they exhibit electric dipole moment even in the absence of an electric field. The centres of positive and negative charges do not coincide in a ferroelectric crystal. Also, the polarization versus electric field plot for a ferroelectric crystal shows a hysteresis loop. This feature is unique as a linear dielectric does not show hysteresis and it is in fact one of the very causes that makes the study of dielectrics such a popular field.

1.2.1 Types of ferroelectrics

Ferroelectric crystals can be classified under two types of transitions - displacive or order disorder.

1. **Displacive:** If propagation of soft phonon mode is allowed in the crystal at transition, then the transition is displacive.
2. **Order-disorder:** If the soft mode is diffusive but not propagating, the phonon does not exist but allows a large amplitude hopping motion between the wells of the order-disorder system.

They can also be classified as normal or relaxor ferroelectrics on the basis of frequency dependence of ϵ_r .

1. **Normal ferroelectrics:** Normal ferroelectrics show either first or second order phase transition at Curie point T_C . They show weak frequency dependence and follow Curie-Weiss law. They show a large remnant polarization as compared to relaxor ferroelectrics. Normal ferroelectrics do not show any hysteresis loop about T_C .
2. **Relaxor ferroelectrics:** Relaxor ferroelectrics show a broad diffuse phase transition at Curie maxima. They also show a strong frequency dependence and follow Curie-Weiss square law. They show a weak remnant polarization as compared to normal ferroelectrics. Relaxor ferroelectrics show a hysteresis loop about T_C .

1.3 Properties of ferroelectrics

1.3.1 Crystal symmetry

Every crystal can be completely described by the 230 crystallographic space groups (symmetry classes). Compared to the space groups, the point groups are only 32. Their detailed classification is shown in the figure below.

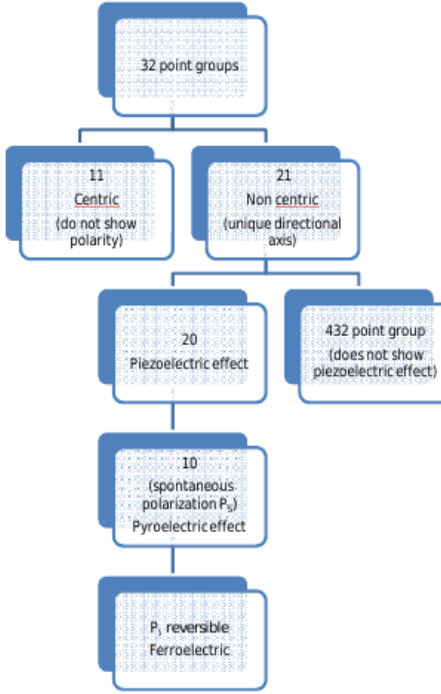


Figure 2: Flowchart showing the division of the 32 point groups

1.3.2 Piezoelectric effect

The word piezoelectricity is derived from the Greek word *piezo* or *piezein* which means to squeeze or press, and *electric* or *electron* which stands for amber, a source of electric charge. Piezoelectric effect refers to the phenomenon of development of electric charge on the surface of a crystal when a mechanical stress is applied. Conversely, a mechanical deformation is produced on application of an electric field. Crystals with no centre of symmetry normally exhibit this effect. Molecules are made up of dipoles. An imaginary

line called polar axis runs through the centres of both positive and negative charges that make up a dipole. In a monocrystal, the polar axes of all the dipoles are oriented in a single direction. In a polycrystal, however, different regions within the material have different polar axes. To produce piezoelectric effect, therefore, a very strong electric field is applied which results in the dipoles facing nearly the same direction.

$$P_i = d_{ijk}s_{jk}(\text{Direct effect}) \quad (1)$$

$$e_{ij} = d_{kij}E_k(\text{Converse effect}) \quad (2)$$

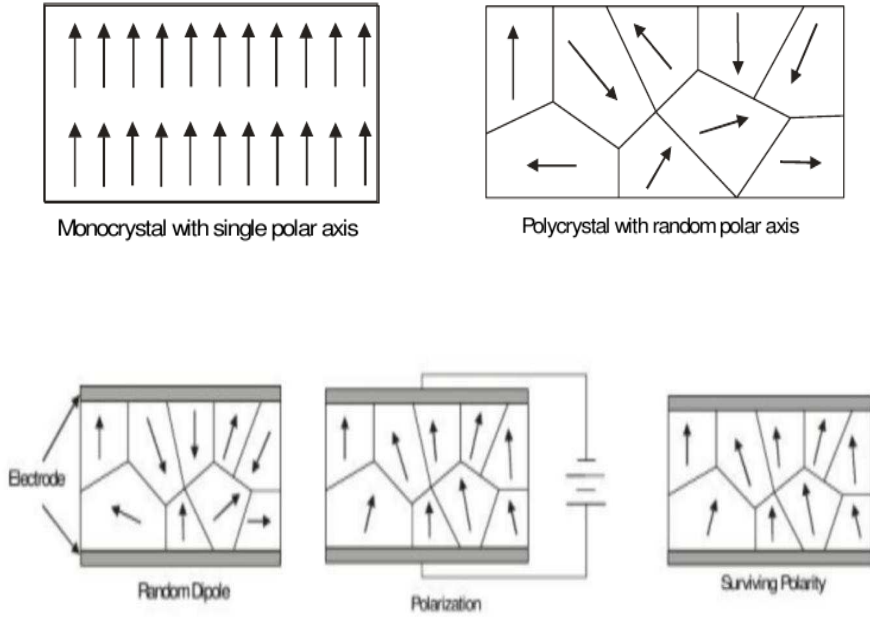


Figure 3: Polarization of ceramic material to generate piezoelectric effect

where P_i is the polarization generated along the i-axis, s_{jk} is the applied stress and d_{kij} is the piezoelectric coefficient. In case of the converse effect, e_{ij} is the strain oriented in a particular direction and E_i is the applied electric field along the i-axis.

1.3.3 Spontaneous polarization and pyroelectric effect

Spontaneous polarization may be defined as the value of dipole moment per unit volume or the value of charge per unit area on the surface perpendicular to the axis of spontaneous polarization. Crystals with a unique polar axis show a spontaneous polarization vector \mathbf{P}_s along this axis. The value of the spontaneous polarization is temperature dependent. This phenomenon of development of charge due to temperature change is called pyroelectric effect. The word pyroelectricity is derived from the Greek word *pyr* which means fire. It was first discovered in Tourmaline crystal by Theophrast in 314 B.C. and was named so by Brewster in 1824.

$$\Delta \mathbf{P}_s = p \times \Delta T \quad (3)$$

where p is the pyroelectric coefficient, ΔT is a small change in temperature and $\Delta \mathbf{P}_s$ is the small change in the spontaneous polarization vector.

1.3.4 P-E hysteresis loop - an important criterion for ferroelectricity

If the magnitude and direction of the spontaneous polarization vector \mathbf{P}_s can be reversed in both magnitude and direction by the application of an external electric field, ferroelectric behaviour results in the corresponding crystal. Therefore, all ferroelectrics are pyroelectric. However, the reverse may not always be true (example: tourmaline shows pyroelectricity but it is not ferroelectric). Next, we consider the concept of domains. Domains are regions of uniform polarization within a ferroelectric crystal. Domains are separated from one another by interfaces called 'domain walls'. To obtain a single domain, electric field is sufficient. It causes motion of the domain walls. A very strong field may result in the polarization getting reversed. This is called 'domain switching'.

The direction of spontaneous polarization can be reversed in ferroelectric materials. This is wherein the difference between pyroelectrics and ferroelectrics lies. This can be best understood from the P-E hysteresis loop. On increasing the electric field, the domains begin to align in the direction of the applied electric field. This considerably increases the polarization (OB). At some high value of the field, the polarization reaches a saturation value (P_{sat}). But, when the external field is removed, surprisingly, the polarization does not drop to zero. At zero external field, some of the domains remain aligned in the positive direction. This is why the crystal shows a remnant polarization P_r . For complete depolarization, a field of magnitude

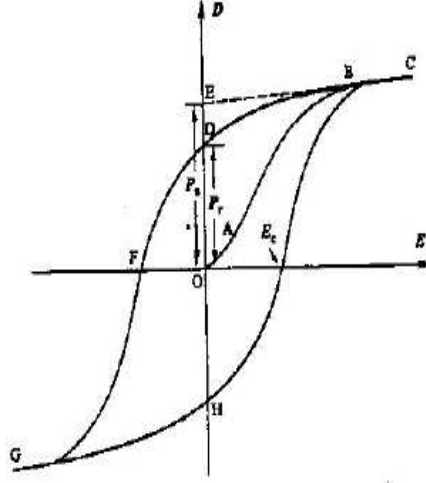


Figure 4: PE hysteresis loop

OF needs to be applied in the negative direction. This negative field required to make the polarization zero is called the coercive field strength E_c . On increasing the field to a higher value in the negative direction, the direction of polarization flips and a hysteresis loop is obtained. The value of the spontaneous polarization \mathbf{P}_s (OE) is obtained by extrapolating the curve onto the polarization axes (CE).

1.3.5 Phase transition in ferroelectrics

All ferroelectrics undergo phase transitions at a temperature called the Curie point. Below the Curie point, the crystal remains ferroelectric, but above it, it loses ferroelectric behaviour. On decreasing temperature, the transition is from non-ferroelectric to ferroelectric phase. If, however, more than one ferroelectric phases exist, the temperature at which a crystal transforms from one ferroelectric phase to another is called transition temperature. The figure below illustrates the behaviour of $BaTiO_3$ as it is cooled from the paraelectric cubic phase to the ferroelectric tetragonal, orthorhombic and rhombohedral phases. At every transition temperature including the Curie point, all thermodynamic properties including dielectric, elastic, optical, and thermal constants show an anomalous behaviour, the reason being distortion

in the structure of the crystal as the temperature changes. The temperature dependence of the dielectric constant, ϵ_r , above the Curie point ($T > T_C$) in ferroelectrics is governed by the Curie-Weiss law:

$$\epsilon = \epsilon_0 + \left(\frac{C}{T - T_0} \right) \quad (4)$$

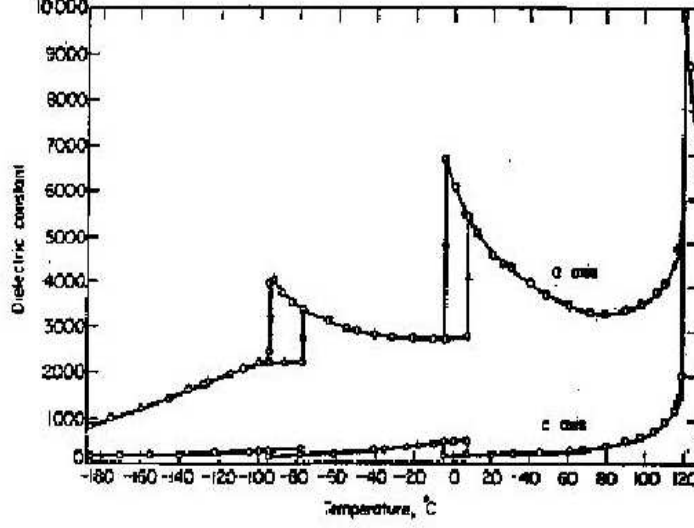


Figure 5: Phase transition in $BaTiO_3$

where ϵ is the permittivity of the material, ϵ_0 is the permittivity of vacuum. C is the Curie constant and T_0 is the Curie temperature. The Curie temperature is different from the Curie point T_C . T_0 is a formula constant obtained by extrapolation whereas T_C is the temperature at which the material changes its structure. $T_0 < T_C$ corresponds to first order transitions and $T_0 = T_C$ corresponds to second order transitions.

1.3.6 Structure of ferroelectrics

Ferroelectrics are grouped under four main structures:

Corner sharing octahedra: Many ferroelectric crystals are made up of mixed oxides containing corner sharing octahedra of O^{2-} ions. There is a cation B^{b+} inside each octahedron (b varies from 3 to 6). The space between the octahedra are occupied by A^{a+} ions (a varies from 1 to 3). Normally, the

geometric centres of A^{a+} , B^{b+} , and O^{2-} coincide giving rise to a non-polar lattice. When the lattice gets polarized, the A and B centres displace with respect to the O^{2-} ions so that the lattice becomes polarized. The corner sharing octahedra includes the perovskite type compounds, tungsten bronze type compounds, bismuth oxide layer structured compounds and pyrochlore.

1. **Perovskites:** A perovskite structure refers to any material with the same type of crystal structure as $CaTiO_3$ (calcium titanium oxide). Perovskites are named after the Russian mineralogist L.A.Perovski. The general chemical formula of perovskites is ABO_3 where A and B are two cations of two different sizes and O is an anion that is bonded to both. The A atoms are larger than the B atoms. Examples of piezoelectric (including ferroelectric) materials that possess this kind of structure are Barium Titanate ($BaTiO_3$), Lead Titanate ($PbTiO_3$), Lead Zirconate Titanate (PZT), Lead Lanthanum Zirconate Titanate (PLZT), Lead Magnesium Niobate (PMN), Potassium Niobate ($KNbO_3$), Potassium Sodium Niobate ($K_xNa_{1-x}NbO_3$) and Potassium Tantalate Niobate ($K(Ta_xNb_{1-x})O_3$). The ferroelectric to be discussed later on, Bismuth Sodium Titanate (BNT) also has the perovskite structure.

The cubic unit cell of a perovskite has the type 'A' atoms at its corner positions (0,0,0), the type 'B' atom at the body centre position ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and the oxygen atoms at the face centred positions ($\frac{1}{2}, \frac{1}{2}, 0$). The orthorhombic and the tetragonal phases are the most common non-cubic variants. The most common research field in material science has been on compounds exhibiting a perovskite structure. This is mainly due to the fact that perovskites show many intriguing properties like ferroelectricity, superconductivity, charge ordering, spin dependent transport, high thermopower etc. These compounds are used as sensors and actuators and are candidates for memory devices and spintronics applications. Yttrium Barium Copper Oxide (YBCO) is an example of a perovskite exhibiting superconductivity.

2. **Tungsten bronze type compounds:** This type of crystals have a structure similar to tetragonal tungsten bronze K_xWO_3 ($x > 1$). The structure is fairly open. This allows substitution with a wide range of cations and anions without loss of ferroelectric behaviour.
3. **Bismuth oxide layer structured ferroelectrics:** The two most important piezoelectric materials with this type of structure are bismuth titanate ($Bi_4Ti_3O_{12}$) and lead bismuth niobate ($PbBi_2Nb_2O_9$).

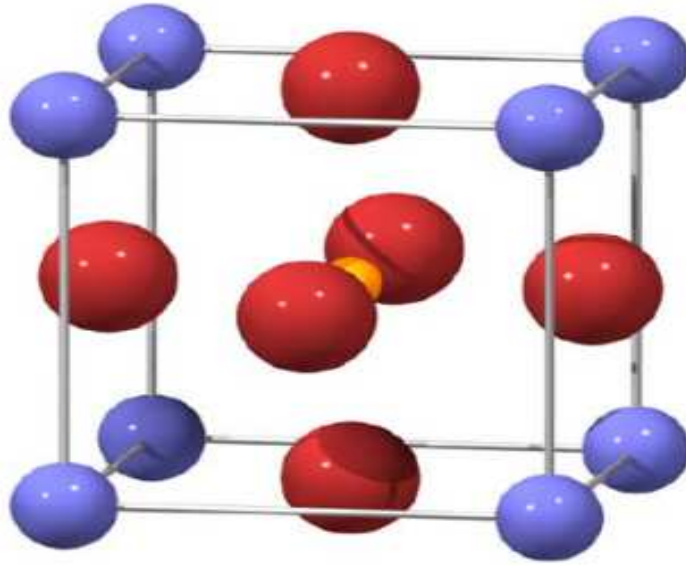


Figure 6: Perovskite structure: Corner atoms-A, atoms at face centre-O, atom at body diagonal-B

These compounds have plate like crystal structure which leads to a high anisotropy in ferroelectric properties. These compounds do not show very high piezoelectric properties due to their low poling efficiency.

4. **Pyrochlore:** The pyrochlore crystal structure describes materials of the type $A_2B_2O_6$ and $A_2B_2O_7$ where the A and B species are generally rare earth or transition metal species (example: $Y_2Ti_2O_7$). The pyrochlore structure is a super structure derivative of the simple fluorite structure ($AO_2 = A_4O_8$, where the A and B cations are ordered along the $\langle 110 \rangle$ plane). These systems are particularly susceptible to geometrical frustration and magnetic effects.

2 MATERIAL SELECTION

2.1 Literature review

Bismuth Sodium Titanate (BNT) was first described by Smolenskii *et. al* in 1961[2]. Thomas and Jones (2002) reported that BNT is a rhombohedral ferroelectric perovskite at room temperature and subsequently changes to tetragonal and then cubic on heating. Initial dielectric and optical property measurements of BNT were reported in the 1990's by many sources. BNT is a promising candidate in the field of piezoelectric applications due to its high piezoelectric constant and high Curie temperature. It is importantly most suitable for ultrasonic applications on account of its low acoustic impedance that ensures maximum efficiency.

Lead based materials have dominated the piezoelectric applications industry for a long time. However, serious environmental concerns are being raised due to the toxic nature of lead. This has led to the emergence of new lead free ceramics like BNT.

2.2 Reasons for selection of BNT

Bismuth Sodium Titanate exhibits strong ferroelectric properties. This material has a fairly high T_C of $320^\circ C$. BNT based materials show high anisotropic electromechanical coupling property and a high frequency constant. Reported value of dielectric constant is 2905[9]. This makes BNT suitable for ultrasonic applications. For the same volume of a material, BNT based materials have the advantage of creating a higher frequency due to their high frequency constant as compared to lead based piezoelectric ceramics (useful in the field of electronic devices).

3 OPTIMIZATION OF SYNTHESIS ROUTES AND EXPERIMENTAL TECHNIQUES

The ferroelectric material bismuth sodium titanate (BNT) was prepared by both the solid state as well as the chemical routes[1,3,4]. It is therefore, deemed necessary to give a general description of the methods of fabrication of ferroelectric materials. Every single step that is involved holds extreme importance and we shall take them up one by one. The description shall begin with the steps of the solid state route followed by the description of the chemical route.

3.1 Solid state synthesis

It is the cheapest route available for synthesis. The raw materials required for synthesis are economical and easily available. Formation of very stable product species through highly energetic reactions takes place in this synthesis method. Rapid synthesis takes place. Reaction conditions and particle sizes of product can be easily controlled. The steps of solid state synthesis are as follows:

3.1.1 Selection of raw materials

The selection of raw materials should be done carefully. The raw materials should be of high purity. The particle size of the powders should be in the sub-micron range for the solid phase reactions to occur by atomic diffusion. Generally, the raw materials selected in this process are oxides (or, carbonates), so, this process is also known as the *oxide mixing technique*. The raw materials selected for the preparation of BNT were Sodium Carbonate (Na_2CO_3), Bismuth Oxide (Bi_2O_3), and Titanium Dioxide (TiO_2).

3.1.2 Stoichiometric weighing

The raw materials selected are weighed according to the calculated stoichiometry. It is very important to maintain the stoichiometry during the course of the solid state reaction. A difference in stoichiometry can result in a change of the desired properties.

3.1.3 Mixing

Mixing can be done either by mechanical methods or by chemical methods. Mechanical methods involve mixing the raw materials in a ball mill or attrition mill for a short time. Chemical mixing, however, is a far better process as it maintains the homogeneity of the raw materials and is done by precipitating the precursors in the same container in which the raw materials are kept after weighing.

3.1.4 Calcination

Calcination involves the heating of the mixed raw materials to any temperature below its melting point to effect a thermal decomposition or a phase transition. During the process of calcination, the volatile components of the mixture are removed. The solid state phase reaction takes place in this step

between the constituents of the mixture giving the ferroelectric phase. The calcination temperature should be carefully chosen as it affects the density and hence the electromechanical properties of the final product. The higher the calcining temperature, the better the homogeneity and density of the final ceramic product. Proper calcination at the right temperature gives the best electrical and mechanical properties.

3.1.5 Grinding

After calcination, due to the solid phase reaction that takes place, the final product becomes lumpy. Grinding is done to reduce the lumps to fine powder.

3.1.6 Binder addition

A small amount of binder, usually poly vinyl alcohol, is added to the calcined product to hold the particles together. Binders aid in the granulation of the powder and provide strength in the green body.

3.1.7 Shaping

In this step, the desired shape can be given to the material. The methods include powder compaction, slip casting and extrusion. In the powder compaction method, the powder is placed under high pressure to get the desired shape. Slip casting is used to make large number of exact replicas of an original model. Extrusion is used to get the shape with fixed cross-sectional profile.

3.1.8 Binder burn out

The binder burn out stage takes place just before sintering. In this step, the grain body is heated in between 500 - 600°C to remove the polymer binder from the ceramic material.

3.1.9 Sintering

After the binder burn out stage, sintering is done. It is a process in which the ceramic material is heated at a high temperature (less than the melting temperature) to achieve the desired microstructure. Microstructure, in this context, refers to density, grain shape, grain size and distribution, porosity, pore size and distribution. The sintering temperature and time should be

optimum for proper densification to occur without abnormal growth. Densification generally occurs by the reduction of surface energy as the free surfaces of particles disappear (i.e., sintering is accelerated with decreasing particle size of the raw powder). For fine powders, the necessary diffusion length of the atoms for sintering becomes shorter, which accelerates pore diffusion. This results in high density ceramics. Densities of ferroelectrics increases with sintering temperature. This is a normal trend. At sintering temperature, accelerated diffusion of the constituent atoms on the fine particle surfaces takes place due to the surface energy (surface tension) that promotes crystal bonding at the contact interface between the two adjacent particles and provides sufficient mechanical strength to the ceramic without significant distortion from the initial moulded shape. The sintering temperature is generally $\frac{2}{3}$ of the melting temperature of the material concerned. The physical properties of the sintered body depends not only on the property of each fine crystalline particle, but also on the grain boundary and the pores. The sintering of oxide ceramics must be carried out in an oxidizing atmosphere or in air. For lead based ceramics, lead loss occurs at temperatures above 800°C . To reduce the lead loss during sintering, the samples are kept in a sealed crucible with a saturated PbO vapour in it.

Microwave sintering: Microwave sintering involves direct heating of the samples with the heating profile from inside to outside. Heating involved is of the volumetric type and is therefore, a fast process. This process causes densification without triggering grain growth and also results in uniform grain morphology[5].

3.1.10 Electroding

Electroding is the process of application of a layer of metallic silver in dispersed liquid or paste form on the surface of the sintered pellets. The silver should adhere very strongly to the ceramic. It should practically be very thin and should have zero resistance, and a good physical and chemical durability. The silvered pellets are then heated to form a continuous conducting layer intimately bonded to the ceramic surface. Electrode adherence is critical. If there is any lack of intimate bonding, the gap between the electrode and the high dielectric constant ceramic acts as a series capacitance of low value.

The final product obtained as a result of solid state synthesis is not very pure and homogeneity is also not well maintained. Also, a very high temperature is required for synthesis. This results in exhaustion of electrical energy. Due to these reasons, we go for chemical route of synthesis in which

homogeneity is also well maintained and less temperature is required for synthesis.

3.2 Chemical synthesis

This method is based on the phase transformation of a sol obtained from metallic alkoxides or organometallic precursors[9]. The main advantages of this process are its versatility and the possibility to obtain high purity metals, the composition of which is perfectly controlled. Densification during sintering is often achieved at a much lower temperature in the chemical mode of synthesis. Ceramics prepared through this route have a variety of applications ranging from optics, electronics, energy, space, (bio)sensors, medicine (eg., controlled drug release) and separation (chromatography). Steps of synthesis are briefly described below.

3.2.1 Selection of raw materials

The chemical method basically involves the principle of solubility. Therefore, raw materials selected should be such that they properly dissolve in the chosen solvents. Typical precursors are metal alkoxides and metal chlorides, which undergo various forms of hydrolysis and polycondensation reactions.

3.2.2 Stoichiometric weighing

The raw materials are weighed according to their calculated stoichiometry.

3.2.3 Dissolution

This step involves dissolving the raw materials in their respective solvents. The solution, after dissolving, must be homogeneous, i.e., a clear solution should be obtained. The solutions are heated if necessary to obtain homogeneity.

3.2.4 Mixing of constituents and drying

All the solutions of the starting materials are mixed together and heated to high temperature. The heating continues until the mixture becomes a clear solution. Further heating is done to obtain the powder residue. Once the entire solution dries up, heating is stopped. This drying process is accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the

distribution of porosity in the gel. The ultimate microstructure of the final component is strongly influenced by changes imposed upon the structural template during this phase of processing.

The powder obtained in this step is then grounded so that the particles are all of uniform size. It is then calcined in the same manner as described in the solid state route. After calcination, binder is added to the powder in order to adhere the particles together. This is followed by shaping the powder into pellets, almost of uniform weight, by the application of high pressure using a hydraulic press. The next step is heating the pellets to about 600°C at which the binder burns out. A firing process is essential to favour further polycondensation and enhance mechanical and structural properties. This is done by sintering which is accompanied by densification and grain growth. Electroding is done in order to measure certain properties of the ceramic.

3.3 X-ray diffraction

X-rays are electromagnetic waves that lie between the ultra violet region and the gamma ray region in the electromagnetic spectrum. The XRD technique involves taking a sample of the material and placing the powdered sample in a holder. The sample is then illuminated with X-rays using $\text{Cu } K_{\alpha}$ radiation of wavelength ($\lambda = 0.15405\text{nm}$). The intensities of the reflected radiation is recorded using a goniometer. XRD of ceramic samples on PW 3020 Phillips diffractometer using $\text{Cu } K_{\alpha}$ ($\lambda = 0.15405\text{nm}$) radiation provided useful information regarding crystal structure, crystallite size and microstrain, unit cell lattice parameters and bravais lattice symmetry, texture or orientation in polycrystalline or powdered solid samples, phase composition of sample etc.

3.4 Scanning electron microscopy

Scanning electron microscopy or SEM gives the topography and grain morphology of sintered samples. A scanning electron microscope images the sample surface by scanning it with a high energy beam of electrons in raster scan (rectangular pattern of image capture and reconstruction in television) pattern. Raster graphics involves the pattern of image storage and transmission used in most computer bitmap image systems. The types of signals produced by SEM include secondary electrons, back scattered electrons, characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. It is a useful tool for microstructure inspection

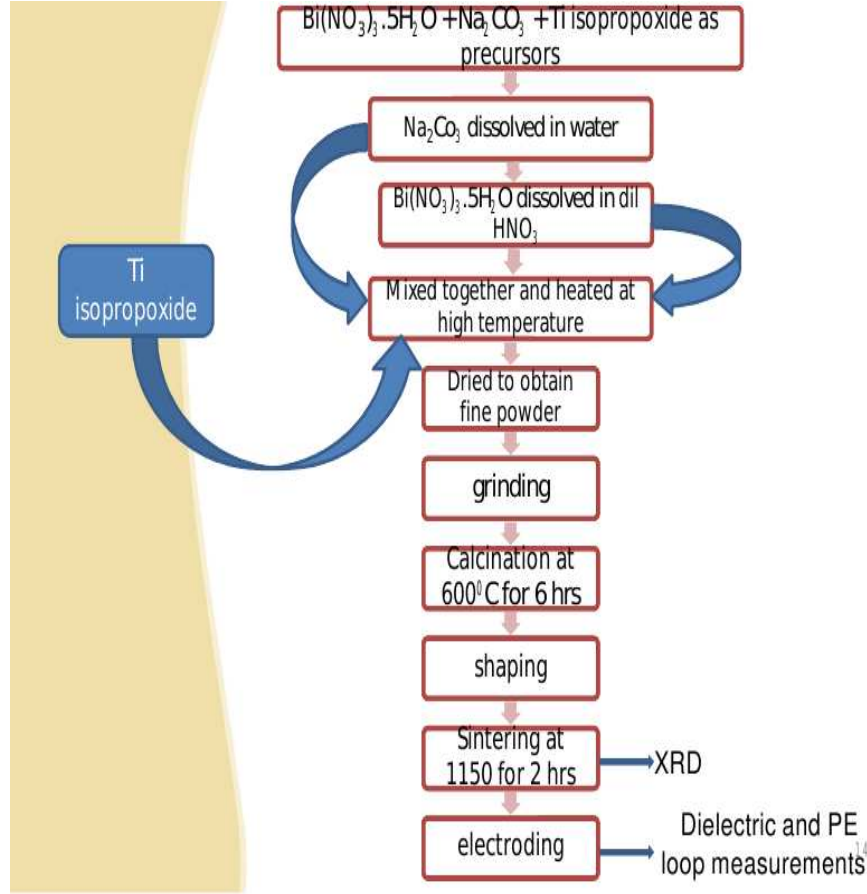


Figure 7: Flowchart showing chemical method of synthesis of a ceramic material

of ferroelectric ceramics. Microstructure of sintered samples were observed using JEOL T-330 scanning electron microscope.

3.5 Study of dielectric properties

Ferroelectric ceramics have a wide range of dielectric constants, from several hundreds to several thousands. The LCR meter is used to study the variation of dielectric constant and dielectric loss with temperature, as well as with frequency. The LCR meter is a piece of electronic test equipment used to measure the inductance, capacitance and resistance of a dielectric. These quantities are determined from the impedance of the sample. The

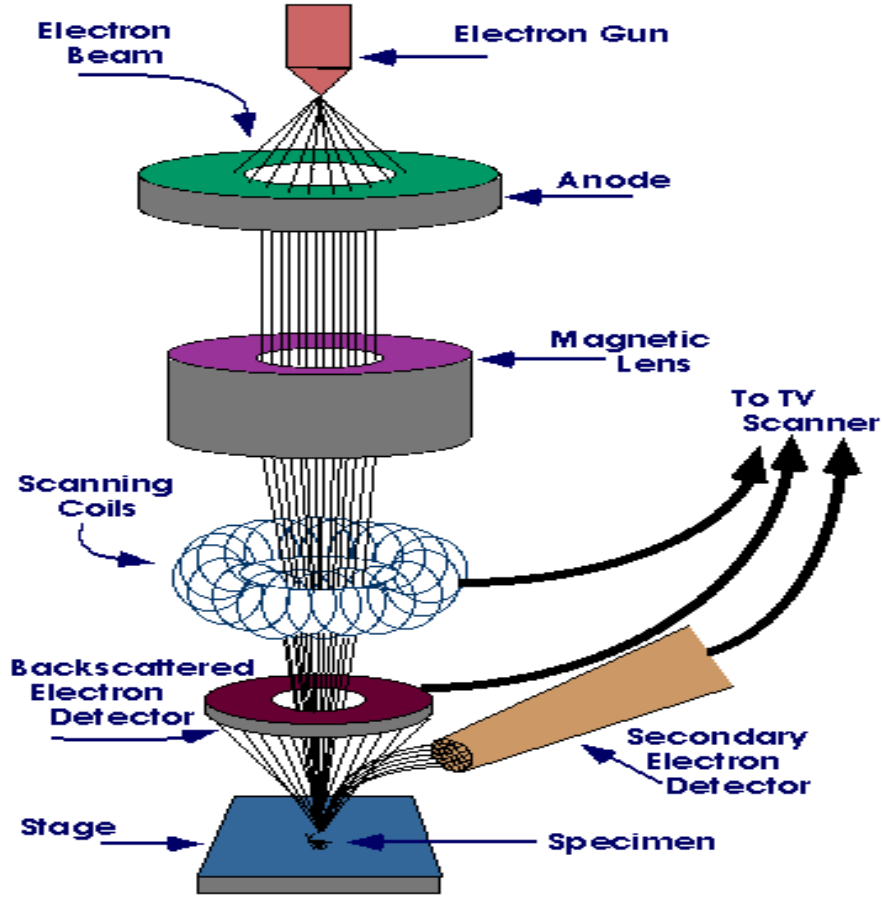


Figure 8: Schematic of scanning electron microscope

device under test (DUT) is subjected to an a.c voltage. The meter detects the voltage over, and the current through the DUT, and subsequently the impedance. Observations were made using a computer interfaced HIOKI 3532-50 LCR-HITESTER.

3.6 PE loop

PE loop or hysteresis loop observations were made using a conventional Sawyer-Tower circuit. The voltage is signalled by the signal generator. Its direction is reversed at high frequency, and the voltage across the reference capacitor is measured. The capacitor and the ferroelectric sample are in se-

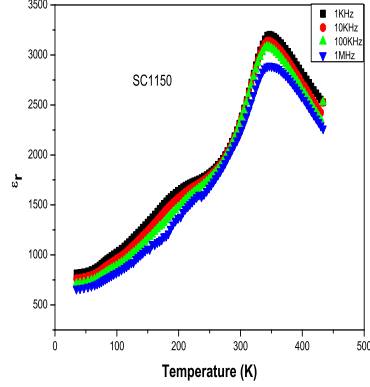


Figure 9: Dielectric constant versus temperature plot of BNT sample synthesized by solid state route and sintered using conventional sintering technique

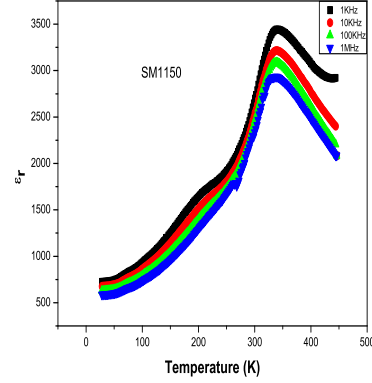


Figure 10: Dielectric constant versus temperature plot of BNT sample synthesized by solid state route and sintered using microwave sintering technique

ries and therefore, have the same charge. The polarization in the oscillating field can be plotted by representing the voltage applied to the material on the X-axis and the surface charge on the Y-axis. Capacitance of the reference capacitor is higher than the capacitance on the ferroelectric sample, so most of the voltage lies on the ferroelectric itself.

4 EXPERIMENTAL PROCEDURE

Bismuth sodium titanate was prepared by the solid state route. Sodium carbonate, Na_2CO_3 , bismuth oxide, Bi_2O_3 and titanium dioxide TiO_2 were used as the starting materials. Stoichiometric proportions of the precursors were taken and ball milled for 8 hours. The resultant wet mixture was then dried following which it was calcined at $750^\circ C$. XRD of the calcined sample yielded monoclinic structure at room temperature and confirmed perovskite phase. 2 percent poly vinyl alcohol (binder) was added to calcined BNT. This was followed by conventional sintering at $1150^\circ C$ for 2 hours and microwave sintering at $1150^\circ C$ for 30 minutes with heating rate of $40^\circ/min$.

Bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$), sodium carbonate (Na_2CO_3) and titanium isopropoxide ($C_{12}H_{28}O_4Ti$) are the precursors that were used for

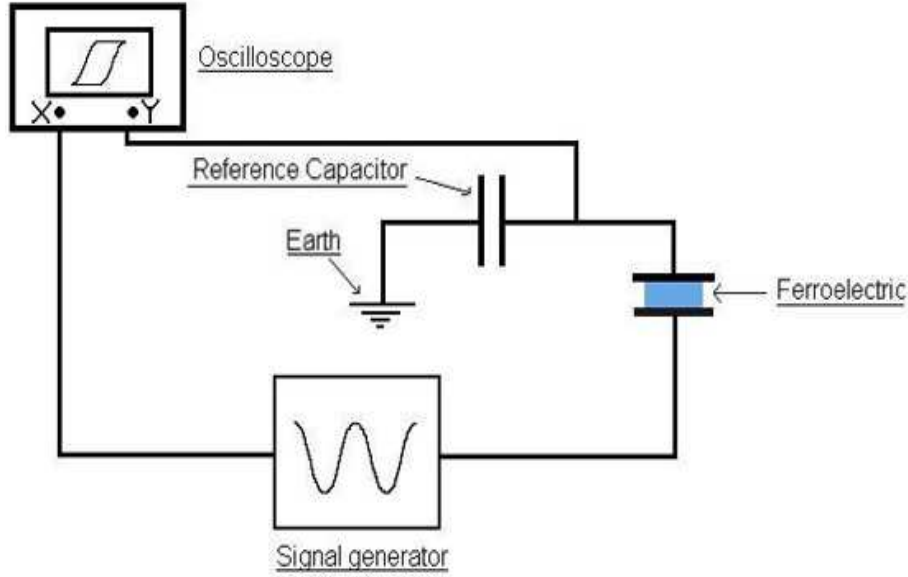


Figure 11: Sawyer-Tower circuit

chemical route synthesis. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in dil. HNO_3 and Na_2CO_3 was dissolved in water. The two solutions were mixed together and Ti isopropoxide was added to the resulting solution. This solution was heated until the solvents evaporated. The residue was cooled and then calcined at 600°C for 6 hours. Sintering was done by the conventional sintering route at 1150°C for 2 hours and by the microwave sintering route at 1150°C for 30 minutes.

5 RESULTS AND DISCUSSIONS

5.1 X-ray diffraction studies

Fig.10 shows that X-ray powder diffraction measurements confirms single perovskite phase (absence of secondary peaks). BNT crystallizes just before 750°C and crystallization is complete at around 850°C after it has been calcined for 8 hours. The XRD patterns clearly indicate monoclinic structure (JCPDS Card No:46-0001) for both conventional and microwave sintered samples. The lattice parameters in accordance with JCPDS data have been summarized in Table 1.

Sintering method	Synthesis process	Structure	a	b	c	β
Conventional	Chemical	Monoclinic	5.553	6.675	5.520	120.00°
Conventional	Solid state	Monoclinic	5.521	6.641	5.513	120.38°
Microwave	Solid state	Monoclinic	4.199	3.907	2.955	110.10°

Table 1: Structures of conventional and microwave sintered samples synthesized by solid state and chemical routes

Sintering method	Synthesis route	Grain size (μm)
Microwave	Solid state	0.92
Microwave	Chemical	0.78
Conventional	Solid state	1.42
Conventional	Chemical	1.12

Table 2: Comparison of grain sizes of samples sintered by conventional and microwave techniques

5.2 Scanning electron microscopy

Samples synthesized using chemical route maintain greater homogeneity and uniform grain size. Figures show that grain size is uniform. The sample was sintered by conventional method at 1150°C for 2 hours and by microwave method at 1150°C for 30 minutes. Since, in the case of chemically synthesized sample densification occurs at a much lower temperature, fig 12 and fig 14 show melting of grains. However, this high temperature is optimum for the sample synthesized using solid state route. Chemically synthesized sample shows smaller grain size due to homogeneity. Lower sintering temperature and rapid heating in microwave sintered samples restrains grain growth and hence smaller grain size is obtained. This confirms densification without grain growth. Thus, microwave sintering is desirable as compared to conventional sintering.

5.3 Dielectric measurements

Capacitance measurements were taken at different frequencies for the samples after electroding. Dielectric constant ϵ_r is a function of both temperature and frequency. The dielectric constant increases with temperature and finally begins to decrease beyond Curie temperature T_C . The initial increase in ϵ_r can be attributed to the fact that a dielectric sample can

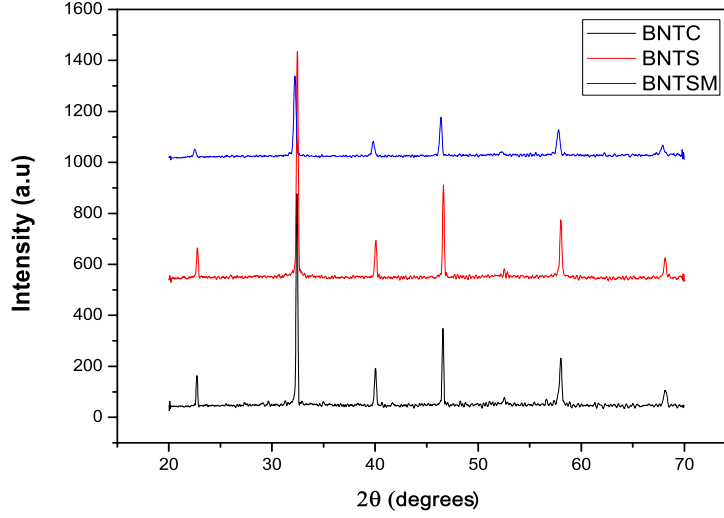


Figure 12: XRD pattern confirming single perovskite phase and monoclinic structure

be polarized and the polarization (space charge polarization) increases with increasing temperature. The polarization increases upto T_C after which it gradually decreases due to the ferroelectric to paraelectric phase transition. It is known that dipoles do not exist in the paraelectric state and therefore cannot contribute to polarization. This results in the decrease of ϵ_r . The upward shifting of T_C with increasing frequency confirms the relaxor nature of the sample[6].

Dielectric loss, $\tan\delta$, increases with temperature due to the increase in conduction of residual current and absorption current[8]. Loss also increases

Sintering method	Synthesis route	ϵ_r	T_C ($^{\circ}\text{C}$)	$\tan \delta$
Microwave	Solid state	3477	340	0.054
Microwave	Chemical	6348	351	0.312
Conventional	Solid state	3222	348	0.056
Conventional	Chemical	5213	332	0.163

Table 3: Variation of ϵ_r , T_C and $\tan \delta$ of BNT samples at 1 kHz

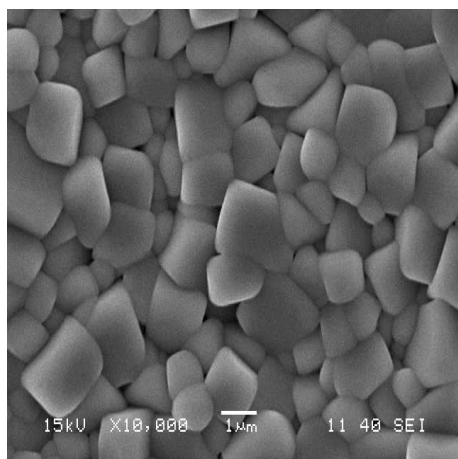


Figure 13: SEM micrograph of BNT sample synthesized by solid state route and sintered using microwave sintering technique

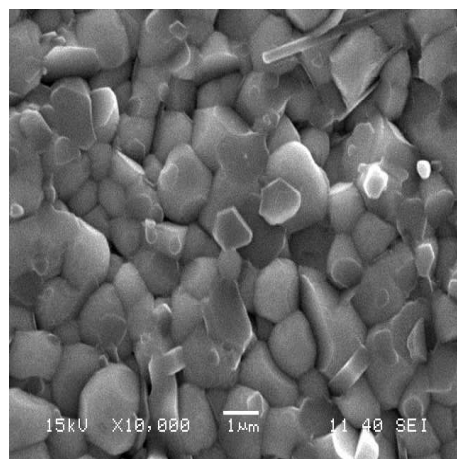


Figure 14: SEM micrograph of BNT sample synthesized by chemical and sintered using microwave sintering technique

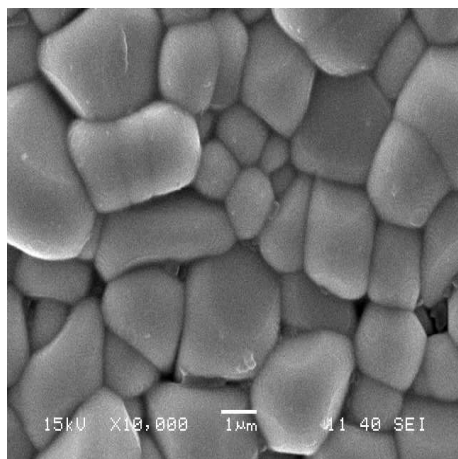


Figure 15: SEM micrograph of BNT sample synthesized by solid state route and sintered using conventional sintering technique

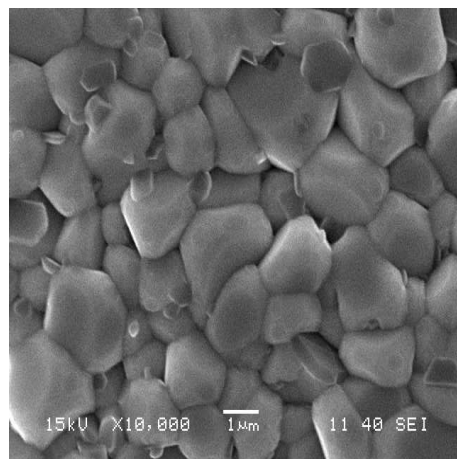


Figure 16: SEM micrograph of BNT sample synthesized by chemical and sintered using conventional sintering technique

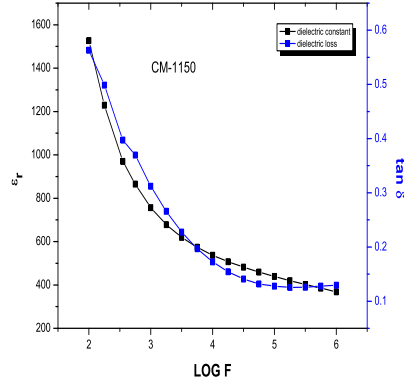


Figure 17: Frequency dependence of dielectric constant and dielectric loss of BNT sample synthesized by chemical route and sintered using microwave sintering technique

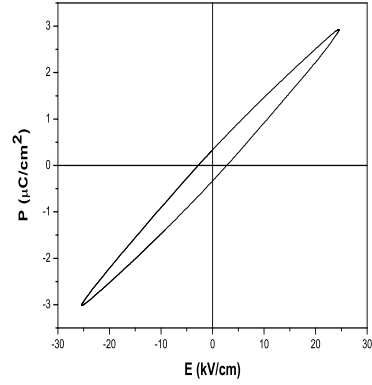


Figure 18: PE hysteresis loop of BNT sample synthesized by solid state route and sintered using conventional sintering technique confirms the ferroelectric nature of the sample

due to the friction of rotating dipoles[8]. Loss, $\tan \delta$ decreases with frequency as the different forms of polarizations start filtering out at increasing frequencies. At low frequencies, $\tan \delta$ is mainly due to dc resistivity.

5.4 PE loop measurements

PE loop of the samples were measured using a conventional Sawyer-Tower circuit. The non-linear nature of the hysteresis loops confirmed the ferroelectric nature of BNT.

6 CONCLUSIONS

Chemical method of synthesis resulted in greater homogeneity of sample and also less grain size. Conventional and microwave sintering methods yielded dense and single phase BNT samples. Microwave sintering has the additional advantage of lower environmental impact. It is also time saving. Microwave sintered samples have smaller grain size due to high densification. Dielectric constant obtained in microwave sintered samples is also high as compared to its conventional counterparts. T_C is also higher in microwave sintered samples. XRD patterns of all the samples yielded monoclinic structure

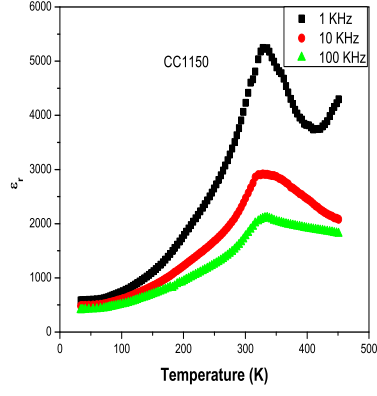


Figure 19: Dielectric constant versus temperature plot of BNT sample synthesized by chemical route and sintered using conventional sintering technique

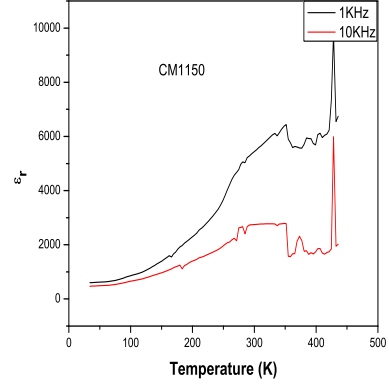


Figure 20: Dielectric constant versus temperature plot of BNT sample synthesized by chemical route and sintered using microwave sintering technique

(JCPDS Card No:46-0001) and single perovskite phase. PE hysteresis loop confirmed ferroelectric nature of the sample.

References

- [1] B.Jaffe, W.R.Cook and H.Jaffe, *Piezoelectric Ceramics* (Academic press, New York,1971).
- [2] G.A.Smolenskii, V.A.Isupv, A.I.Afranovskaya and N.N.Krainik, *J.Sov.Phys.Sol.Stat.***2**, 2651(1961.)
- [3] Ahmad Safari, Rajesh K.Panda, and Victor F.Janas *Ferroelectric Ceramics: Processing, properties and applications*
- [4] K.Uchino, *Ferroelectric devices* (Marcel Dekker, New York, 2000)
- [5] M.Venkatramana, S.Roopas Kiran, N.Ramamanohar Reddy, K.V.Siva Kumar, V.R.Murthy and B.S.Murthy *Journal of Advanced Dielectrics* **1**, 71-77 (2011)
- [6] C.S.Tu, I.G.Siny and V.H.Schmid, *Phys.Rev.B* **49** 11550 (1994)
- [7] S.Rhee, D.Agrawal, T.ShROUT, M.Thumm, *Ferroelectrics* **261**, 15 (2001)
- [8] S.K.S.Parashar, R.N.P.Choudhary and B.S.Murty, *J. App. Phys.* **98** 104305 (2005)
- [9] Jeong Ho.Cho, Yong-Jun Ma, Yong-Hyeon Lee, Myoung-Pyo Chun and Byung-Ik Kim, *Journal of Ceramic Processing Research* **7** 91-94 (2006)